

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-088030

(43)Date of publication of application : 02.04.1996

(51)Int.Cl. H01M 14/00

C08F 20/34

C08L 33/06

H01B 1/06

H01L 31/04

(21)Application number : 06-273057 (71)Applicant : SHOWA DENKO KK

(22)Date of filing : 12.10.1994 (72)Inventor : TAKEUCHI MASATAKA

(30)Priority

Priority number : 06190061

Priority date : 19.07.1994

Priority country : JP

(54) WET SOLAR CELL AND MANUFACTURE THEREOF

(57)Abstract:

PURPOSE: To prevent corrosion of an electrode and electrolyte leakage and easily form as a thin film by coating by using a polymer solid electrolyte as an ion conductive material.

CONSTITUTION: A semiconductor electrode 1 is formed into a film on a transparent conductive board by vapor deposition or coating, and a counter electrode 3 is formed with a conductive material. Both electrodes are bonded

through a spacer 4 so as not to come into contact each other and they are put into a wet solar cell constituting structure. A mixture of ACE or MCE and an oxidation/reduction material is filled in a space formed with the spacer 4, and polymerized by heating and/or irradiation of electromagnetic wave such as light. This polymerizable monomer mixture is formed into a film form to use as a polymer solid electrolyte 2 of a film-shaped polymer. Contact of the electrolyte 2 with electrodes 1, 3 is made good, the electrolyte 2 with high film strength is easily formed, and ion conductivity is enhanced.

LEGAL STATUS [Date of request for examination] 10.05.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3546085

[Date of registration] 16.04.2004

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] It sets to the wet solar battery which has arranged the ion conductivity matter including a oxidation reduction kind between two electrodes at least whose one side of an electrode is semi-conductors, and the ion conductivity matter is a general formula (1).

$\text{CH}_2 = \text{C}(\text{R}_1) \text{CO}[\text{OQ}]_z \text{NHCOOR}_2$ (R1 expresses hydrogen or a methyl group among a formula, and R2 expresses the organic chain containing at least one or more oxyalkylene radicals.) (1) this organic chain -- the shape of a straight

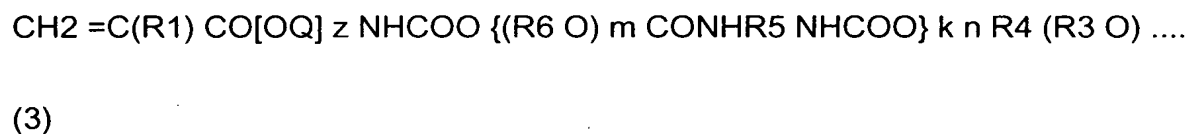
chain, the letter of branching, or cyclic structure -- so-called -- ***** -- one or more elements other than carbon, hydrogen, and oxygen may be contained. Q consists of $-(CH_2)_x-$ and $-[CH(CH_3)]_y-$, and x and y express the alkylene group combined in order of arbitration for the integer of 0, or 1-5. However, x and y are not set to 0 to coincidence. z expresses the integer of 0, or 1-10. Wet solar battery characterized by being a solid polymer electrolyte containing the copolymer which uses as a copolymerization component the polymer and/or this compound which are obtained from a kind of compound chosen from the acryloyl carbamic-acid ester or (meth)acryloyloxy alkyl carbamic-acid ester expressed (meta) at least.

[Claim 2] It sets to the wet solar battery which has arranged the ion conductivity matter including a oxidation reduction kind between two electrodes at least whose one side of an electrode is semi-conductors, and the ion conductivity matter is a general formula (2).



(R₁ expresses hydrogen or a methyl group among a formula, and Q consists of $-(CH_2)_x-$ and $-[CH(CH_3)]_y-$, and expresses the alkylene group which x and y combined in order of arbitration for the integer of 0, or 1-5.) However, x and y are not set to 0 to coincidence. As for R₃, each expresses $-(CH_2)_2-$ or $-CH(CH_3)CH_2-$ independently. R₄ A carbon number is the alkyl group of the range of 1

thru/or 10, and $-\text{CONH}(\text{Q}'\text{O})$ w $\text{COCH}=\text{CH}_2$. Or $-\text{CONH}(\text{Q}'\text{O})$ w $\text{COC}(\text{CH}_3)=\text{CH}_2$ It expresses. Q' consists of $-(\text{CH}_2)_{x'}$ - and $-\text{[CH(CH}_3)]_{y'}$ -, and x' and y' express the alkylene group combined in order of arbitration for the integer of 0, or 1-5. However, x' and y' are not set to 0 to coincidence. n expresses the number of one or more numbers, w and z 0, or 1-10. The acryloyl carbamic-acid ester expressed (meta), (meth)acryloyloxy alkyl carbamic-acid ester, or general formula (3)

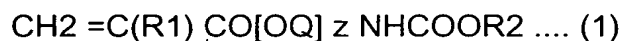


(R_1 expresses hydrogen or a methyl group among a formula, and Q consists of $-(\text{CH}_2)_x$ - and $-\text{[CH(CH}_3)]_y$ -, and expresses the alkylene group which x and y combined in order of arbitration for the integer of 0, or 1-5.) However, x and y are not set to 0 to coincidence. z expresses the integer of 0, or 1-10. R_3 And R_6 Each expresses $-(\text{CH}_2)_2$ - or $-\text{CH(CH}_3)\text{CH}_2$ - independently. R_4 A carbon number is the alkyl group of the range of 1 thru/or 10, and $-\text{CONH}(\text{Q}'\text{O})$ w $\text{COCH}=\text{CH}_2$. Or $-\text{CONH}(\text{Q}'\text{O})$ w $\text{COC}(\text{CH}_3)=\text{CH}_2$ It expresses. R_5 A carbon number 1 thru/or the alkylene group of the range of 20, a propine radical, an arylene radical, Or an oxyalkylene radical is expressed, as for Q' , each consists of $-(\text{CH}_2)_{x'}$ - and $-\text{[CH(CH}_3)]_{y'}$ - independently, and x' and y' express the alkylene group combined in order of arbitration for the integer of 0, or 1-5. However, x'

and y' are not set to 0 to coincidence. n, m, and k express the number of one or more numbers, w and z0, or 1-10, respectively. Wet solar battery characterized by being a solid polymer electrolyte containing the copolymer which uses the polymer and/or this compound which are obtained from a kind of compound chosen from the compound expressed at least as a copolymerization component.

[Claim 3] The wet solar battery according to claim 1 or 2 with which the plasticizer is added by the solid polymer electrolyte.

[Claim 4] General formula (1)



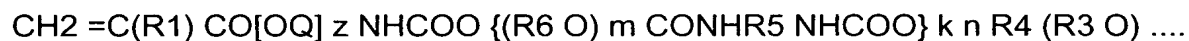
(R1 expresses hydrogen or a methyl group among a formula, and R2 expresses the organic chain containing at least one or more oxyalkylene radicals.) this organic chain -- the shape of a straight chain, the letter of branching, or cyclic structure -- so-called -- ***** -- one or more elements other than carbon, hydrogen, and oxygen may be contained. Q consists of $-(\text{CH}_2)_x-$ and $-\text{CH}(\text{CH}_3)_y-$, and x and y express the alkylene group combined in order of arbitration for the integer of 0, or 1-5. However, x and y are not set to 0 to coincidence. z expresses the integer of 0, or 1-10. The manufacture approach of the wet solar battery characterized by to put in the polymerization nature monomer mixture with which the plasticizer was added by the polymerization nature monomer mixture or this which contains at least a kind of compound

chosen from the acryloyl carbamic-acid ester or (meth)acryloyloxy alkyl carbamic-acid ester expressed (meta) in the structure of a wet solar battery, or to arrange on a base material, and to carry out the polymerization of this polymerization nature monomer mixture.

[Claim 5] General formula (2)



(R₁ expresses hydrogen or a methyl group among a formula, Q consists of -(CH₂)_x- and -[CH(CH₃)]_y-, and x and y express the alkylene group combined in order of arbitration for the integer of 0, or 1-5.) However, x and y are not set to 0 to coincidence. As for R₃, each expresses -(CH₂)₂- or -CH(CH₃)CH₂- independently. R₄ A carbon number is the alkyl group of the range of 1 thru/or 10, and -CONH(Q'O)_wCOCH=CH₂. Or -CONH(Q'O)_wCOC(CH₃)=CH₂ It expresses. Q' consists of -(CH₂)_{x'}- and -[CH(CH₃)]_{y'}-, and x' and y' express the alkylene group combined in order of arbitration for the integer of 0, or 1-5. However, x' and y' are not set to 0 to coincidence. n expresses the number of one or more numbers, w and z 0, or 1-10. The acryloyl carbamic-acid ester expressed (meta), (meth)acryloyloxy alkyl carbamic-acid ester, or general formula (3)



(3)

(R1 expresses hydrogen or a methyl group among a formula, Q consists of $-(CH_2)_x-$ and $-[CH(CH_3)]_y-$, and x and y express the alkylene group combined in order of arbitration for the integer of 0, or 1-5.) However, x and y are not set to 0 to coincidence. z expresses the integer of 0, or 1-10. R3 And R6 Each expresses $-(CH_2)_2-$ or $-CH(CH_3)CH_2-$ independently. R4 A carbon number is the alkyl group of the range of 1 thru/or 10, and $-CONH(Q'O)wCOCH=CH_2$. Or $-CONH(Q'O)wCOC(CH_3)=CH_2$ It expresses. R5 A carbon number 1 thru/or the alkylene group of the range of 20, a propine radical, an arylene radical, Or an oxyalkylene radical is expressed, Q' consists of $-(CH_2)_{x'}-$ and $-[CH(CH_3)]_{y'}-$, and x' and y' express the alkylene group combined in order of arbitration for the integer of 0, or 1-5. However, x' and y' are not set to 0 to coincidence. n, m, and k express the number of one or more numbers, w and z0, or 1-10, respectively.

Polymerization nature monomer mixture which contains a kind of compound chosen from the compound expressed at least, Or the manufacture approach of the wet solar battery characterized by having the process which puts in the polymerization nature monomer mixture with which the plasticizer was added by this in the structure for a wet solar-battery configuration, or arranges on a base material, and carries out the polymerization of this polymerization nature monomer mixture.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the solid-state mold wet solar battery which used for the electrolyte layer the solid polymer electrolyte containing the macromolecule with which the oligo oxy-alkyl side chain and bridge formation radical which have a urethane bond were introduced of high ion conductivity, and its manufacture approach.

[0002]

[Description of the Prior Art] The application to components, such as a solid state of a wet solar battery, all solid-state primary, a rechargeable battery, and an electric double layer capacitor, is briskly tried as a new ion conductor which changes a solid electrolyte to the conventional electrolytic solution in the flow of downsizing in the ionics field, and all solid states.

[0003] A wet solar battery is also called an electrochemical photoelectric cell, and the research latest [many] is made as compared with the solid-state solar battery used now from the reasons of simple [in respect of / -- the ease of junction formation of a semi-conductor interface / electrolyte and the room of use

of a polycrystal semi-conductor are large -- / component creation], a well head, etc. For example, cadmium chalcogenide / polysulfide water-solution system wet solar battery is reported by J.Electrochem.Soc.Vol.134, No.5, and P1064-1070 (1987). An efficient thing called 14.9% of quantum efficiency is obtained by the collection of the Chemical Society of Japan lecture summaries, and one E404 with ITO/HBr-Br₂ / silicon wet solar battery in autumn of 1992.

[0004] In the wet solar battery using a current electrolytic solution, since it is easy to generate the liquid spill to the corrosion of an electrode, and the components exterior, or the elution of electrode material, a problem is in dependability over a long period of time. The thing using a solid electrolyte does not have such a problem to it, and thin-film-izing is also easy and it is [it excels also in thermal resistance further and] advantageous also to a wet solar-battery making process. Especially the thing that used the solid electrolyte which used the macromolecule as the principal component has the merit that the flexibility of a component can process increase and various configurations. For example, at the 10th Kokusai Electric automobile symposium (1990), they are polyethylene oxide / KI/I₂. Or the wet solar battery which used polyethylene oxide / Na₂ S / polysulfide for the redox electrolyte layer is proposed. However, since what has so far been examined had the low ionic conductivity of a solid polymer electrolyte, the extraction current had left the problem that it was small and

quantum efficiency was low.

[0005] Although it is indicated as an example of these giant-molecule solid electrolytes in "the 319th volume (Br.Polym.J) of a British polymer journal, 137 pages, and 1975" that the composite of polyethylene oxide and an inorganic alkali-metal salt shows ion conductivity, the ion conductivity in the room temperature is as low as ten to 7 S/cm.

[0006] Recently, the tandem-type giant molecule which introduced oligo oxyethylene into the side chain raises the thermal-motion nature of the oxyethylene chain which is bearing ion conductivity, and many things for which ion conductivity is improved are reported. For example, the example which compound-ized the alkali-metal salt to what added oligo oxyethylene to the side chain of polymethacrylic acid is indicated in "journal OBU physical chemistry (J. Phys.Chem), the 89th volume, 987 pages, and 1984." Furthermore, the example which compound-ized the alkali-metal salt to the polyphosphazene which has an oligo oxyethylene side chain is indicated in "a journal OBU American society (J. Am.Chem.Soc.), the 106th volume, 6854 pages, and 1984."

[0007] The ionic conductivity of these solid polymer electrolytes in which the example was shown above is level low double or more figures in addition as compared with the electrolytic solution, although improved to 10^{-4} - 10^{-5} S/cm with the value in a room temperature at last by the tandem-type macromolecule

system. Moreover, if it becomes low temperature 0 degree C or less, ionic conductivity will fall further extremely.

[0008] Moreover, although it is possible to add a plasticizer etc. to these solid polymer electrolytes, and to make ionic conductivity high comparatively, since a fluidity will be given, it cannot be dealt with as a perfect solid-state, but is inferior to film reinforcement or membrane formation nature, and there is also a problem of being easy to connect too hastily when it uses for a component.

[0009] Furthermore, when using these solid polymer electrolytes as a thin film and including in a wet solar battery, difficulty is in the workability in fields with an electrode, such as compound-izing and adhesive reservation, and other troubles on a manufacturing technology will be generated.

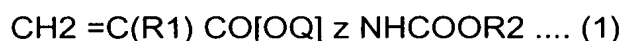
[0010]

[Problem(s) to be Solved by the Invention] Also when it is made into the film, reinforcement of this invention is good, the ionic conductivity in a room temperature and low temperature is high, and by using the solid polymer electrolyte excellent in workability, thin-film-izing is easy and it can operate with efficient and a high current, and cycle nature is good and it aims at developing the wet solar battery excellent in dependability.

[0011]

[Means for Solving the Problem] For this invention, it sets to the wet solar battery

which has arranged the ion conductivity matter including a oxidation reduction kind between two electrodes at least whose one side of an electrode is semi-conductors, and the ion conductivity matter is a general formula (1).



(R1 expresses hydrogen or a methyl group among a formula, and R2 expresses the organic chain containing at least one or more oxyalkylene radicals.) this organic chain -- the shape of a straight chain, the letter of branching, or cyclic structure -- so-called -- ***** -- one or more elements other than carbon, hydrogen, and oxygen may be contained. Q consists of $-(\text{CH}_2)_x-$ and $-\text{CH}(\text{CH}_3)_y-$, and expresses the alkylene group which x and y combined in order of arbitration for the integer of 0, or 1-5. However, x and y are not set to 0 to coincidence. z expresses 0, or 1-10.

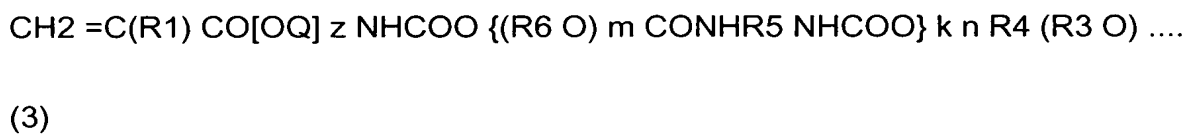
[0012] The wet solar battery characterized by being a solid polymer electrolyte containing the copolymer which uses the polymer and/or this compound which are obtained from a kind of compound which came out and was chosen from the acryloyl carbamic-acid ester expressed, acryloyloxy alkyl carbamic-acid ester (it is called Following ACE.) or methacryloyl carbamic-acid ester, and methacryloyloxy alkyl carbamic-acid ester (it is called Following MCE.) at least as a copolymerization component, and [0013] The ion conductivity matter including a oxidation reduction kind is arranged between two electrodes at least

whose one side of an electrode is semi-conductors, it sets to a wet solar battery, and the ion conductivity matter is a general formula (2).



[0014] (R₁ expresses hydrogen or a methyl group among a formula, and Q consists of -(CH₂)_x- and -[CH(CH₃)]_y-, and expresses the alkylene group which x and y combined in order of arbitration for the integer of 0, or 1-5.) However, x and y are not set to 0 to coincidence. As for R₃, each expresses -(CH₂)₂- or -CH(CH₃)CH₂- independently, and "each is " means that n R₃ of n (R₃ O) can choose the radical of -(CH₂)₂- and -CH(CH₃)CH₂- as arbitration independently, respectively in [this invention. Following R₆ It sets and is the same.] R₄ A carbon number is the alkyl group of the range of 1 thru/or 10, and -CONH(Q'O) w COCH=CH₂. Or -CONH(Q'O) w COC(CH₃)=CH₂ Expressing, Q' consists of -(CH₂)_{x'}- and -[CH(CH₃)]_{y'}-, and x' and y' express the alkylene group combined in order of arbitration for the integer of 0, or 1-5. However, x' and y' are not set to 0 to coincidence. n expresses one or more numbers, w and z0, or 1-10.

[0015] ACE come out of and expressed, MCE, or a general formula (3)



[0016] (R₁ expresses hydrogen or a methyl group among a formula, and Q

consists of $-(CH_2)_x-$ and $-[CH(CH_3)]_y-$, and expresses the alkylene group which x and y combined in order of arbitration for the integer of 0, or 1-5.) However, x and y are not set to 0 to coincidence. z expresses the integer of 0, or 1-10. R3 And R6 Each expresses $-(CH_3)_2-$ or $-CH(CH_3)CH_2-$ independently. R4 A carbon number is the alkyl group of the range of 1 thru/or 10, and $-CONH(Q'O)wCOCH=CH_2$. Or $-CONH(Q'O)wCOC(CH_3)=CH_2$ It expresses. R5 A carbon number 1 thru/or the alkylene group of the range of 20, a propine radical, an arylene radical, Or an oxyalkylene radical is expressed, Q' consists of $-(CH_2)_x-$ and $-[CH(CH_3)]_y-$, and x and y express the alkylene group combined in order of arbitration for the integer of 0, or 1-5. However, x and y are not set to 0 to coincidence. n, m, and k express the number of one or more numbers, w and z0, or 1-10, respectively.

[0017] The compound come out of and expressed, since -- it is obtained from a kind of compound chosen at least -- a polymer And/or, this compound The copolymer used as a copolymerization component The polymerization nature monomer mixture with which the plasticizer was added by the polymerization nature monomer mixture or this which contains a kind of compound chosen from ACE expressed with the wet solar battery characterized by being the included solid polymer electrolyte, and said general formula (1), or MCE at least The manufacture approach of the wet solar battery characterized by putting in in the

structure of a wet solar battery, or arranging on a base material, and carrying out the polymerization of this polymerization nature monomer mixture, and [0018] The polymerization nature monomer mixture which contains at least a kind of compound chosen from the compound expressed with ACE or MCE expressed with said general formula (2), or said general formula (3), Or the polymerization nature monomer mixture with which the plasticizer was added by this was put in in the structure for a wet solar-battery configuration, or it has arranged on a base material, and the above-mentioned purpose was attained by developing the manufacture approach of the wet solar battery characterized by having the process which carries out the polymerization of this polymerization nature monomer mixture.

[0019] In addition, in this invention, the oligo oxyalkylene and polyoxyalkylene containing at least one or more oxyalkylene radicals are also contained in an expression called oxy-alkyl, and a bridge formation chain is also contained in the expression a "side chain", and oligo oxy-alkyl expresses an oxyalkylene chain including at least one or more structural units which consist of $-\text{CH}_2 \text{CH}_2\text{-O-}$ or $-\text{CH}(\text{CH}_3) \text{CH}_2\text{-O-}$.

[0020] The thing which has two or more urethane groups like the compound which has one thru/or two polymerization nature machines by MCE expressed with said general formula (2), ACE, etc. as an example of ACE and MCE which

are the compound expressed with said general formula (1) used by this invention, and the compound expressed with said general formula (3), or the compound with which R of said general formula (1) contains an annular oxyalkylene radical like crown ether is mentioned.

[0021] It is easily obtained by carrying out the pyrogenetic reaction of the methacryloyl isocyanate (henceforth MI) or acryloyl isocyanate (henceforth AI) to which each corresponds, and the oligoalkylene glycol as a synthesis method of ACE or MCE of a compound expressed with the general formula (1) or general formula (2) which is the monomer of the solid polymer electrolyte used for this invention.

[0022] Furthermore, the compound which is expressed with a general formula (3) and which has two or more urethane groups obtains a b-mol product according to the two following reaction schemes by the alkylene glycol [which has two isocyanate radicals like hexamethylene diisocyanate or tolylene diisocyanate / a mols of compounds, a mols of alkylene glycol, and b mols of monoalkyl alkylene glycol] reaction, and is obtained again by subsequently making above-mentioned MI or AI of this product and equimolar react.

[0023]

$a(\text{OCNR}_5\text{NCO}) + a(\text{HO}(\text{R}_6\text{O})_m\text{H})$

$+ b(\text{HO}(\text{R}_3\text{O})_n\text{R}_4) \longrightarrow$ (among a formula, a and b are numbers and have the

relation of $a > b$ and $a/b = k$.) $bHO\{(R_6O)_mCONHR_5NHCOO\} a/b n R(R_3O)_4$
 $HO\{(R_6O)_mCONHR_5NHCOO\} k n R_4(R_3O) + MI \text{ or } AI \rightarrow$ Compound of a
 general formula (3) As another synthesis method of a compound expressed with
 a general formula (3), even if it follows the two following reaction schemes, it can
 manufacture. That is, a d-mol product is obtained at a reaction with c mols of
 compounds and alkylene glycol (c+d) mol which have two isocyanate radicals,
 and there is also an approach to which MI or AI of this product and 2 double mol
 is subsequently made to react.

[0024]

$c(OCNR_5NCO) + (c+d)(HO(R_6O)_mH) \rightarrow dHO\{(R_6O)_mCONHR_5NHCOO\}$
 $c/d m H(R_6O)$ (among a formula, c and d are numbers and have the relation of
 $c > d$ and $c/d = k$.) $HO\{(R_6O)_mCONHR_5NHCOO\} k m H(R_6O) + 2(MI \text{ or } AI) \rightarrow$
 Compound of a general formula (3) [0025] In addition, oligoalkylene glycol and a
 polyalkylene glycol are also contained in the expression "alkylene glycol" in the
 publication of this specification. Moreover, similarly monoalkyl oligoalkylene
 glycol and a monoalkyl polyalkylene glycol are contained in the expression
 "monoalkyl alkylene glycol."

[0026] In the compound expressed with these general formulas (1), the
 compound expressed with a general formula (2) is desirable from the ability to
 introduce more urethane groups and oxyalkylene radicals into the side chain in

the polymer obtained. The copolymer (it is called a (Following M) ACE polymer.) which contains in a component the polymer of ACE and/or MCE or these which are contained in the solid polymer electrolyte used for the wet solar battery of this invention is obtained by carrying out the polymerization of a kind of compound chosen from ACE expressed with said general formula (1), or MCE at least, or carrying out a polymerization, using this compound as a copolymerization component. The general approach using the polymerization nature of the acryloyl radical of these monomers or a methacryloyl radical can be used for a polymerization.

[0027] Namely, these monomers or these monomers, and other polymerization nature compounds, For example, after mixing acrylic ester (meta), acrylamide (meta), N-vinyl acetamide, etc. Radical polymerization catalyst, such as azobisisobutyronitril and benzoyl peroxide, proton acid, such as CF_3COOH , BF_3 , and AlCl_3 etc. -- cationic polymerization catalysts, such as Lewis acid, -- or anionic polymerization catalysts, such as butyl lithium, sodium naphthalene, and a lithium alkoxide, -- using -- a radical and a cation -- or anionic polymerization can be carried out. Moreover, it is [after fabricating this polymerization nature monomer mixture in forms, such as the shape of film,] also possible to carry out a polymerization. (M) When using an ACE polymer for a wet solar battery like this invention, it is advantageous to carry out a polymerization in this way,

especially, after forming polymerization nature monomer mixture.

[0028] Namely, at least a kind of compound and sulfur which are chosen from the compound expressed with ACE, MCE, or the general formula (3) expressed with a general formula (1) or a general formula (2), Oxidation reduction nature matter, such as a selenium, iodine, a bromine, a ferrocene, and a metal ion, is mixed. Depending on the case, a kind of electrolyte like an alkali-metal salt, quarternary ammonium salt, the 4th class phosphonium salt, or a transition-metals salt is mixed at least. Furthermore, depending on the case, addition mixing of other polymerization nature compounds, plasticizers, and/or solvents is carried out, to the bottom of existence of said catalyst or nonexistence, depending on the case, electromagnetic waves, such as heating and/or light, are irradiated and the polymerization of these polymerization nature monomer mixture is carried out. The degree of freedom in the assembly and the processing side of a wet solar battery serves as breadth and a big merit on application by irradiating electromagnetic waves, such as heating and/or light, carrying out a polymerization, after fabricating this polymerization nature monomer mixture in configurations, such as the shape of film, and considering as a film-like polymerization object especially.

[0029] In using a solvent, it is based also on the class of compound expressed with a general formula (1), or the existence of a polymerization catalyst, but if it is

the solvent which does not check a polymerization, what kind of solvent is sufficient, for example, a tetrahydrofuran, an acetonitrile, toluene, etc. can be used. What is necessary is just to usually carry out in 0 to 200 degrees C that what is necessary is just the temperature from which a polymerization arises, although based on the class of compound expressed with a general formula (1) as temperature which carries out a polymerization. Although it is based on the class of compound expressed with a general formula (1) in carrying out a polymerization by electromagnetic wave exposure, initiators, such as benzyl methyl ketal and a benzophenone, are used, and ultraviolet radiation or a gamma ray several mW or more etc. can be irradiated, and can carry out a polymerization, for example.

[0030] (M) ACE polymer used for the wet solar battery of this invention may be a homopolymer of ACE or MCE expressed with a general formula (1) as mentioned above, may be two or more sorts of copolymers, ACE or MCE, or may be a copolymer of a kind of ACE or MCE, and other polymerization nature compounds at least. Moreover, the polymer contained in the solid polymer electrolyte used for the wet solar battery of this invention may be the mixture of applied (M) ACE polymer and other polymers.

[0031] For example, the mixture of (M) ACE polymer and polymers, such as polyethylene oxide, a polyacrylonitrile, polybutadiene, Pori (meta) acrylic ester,

polyphosphazene, a polysiloxane, or polysilane, may be used for the solid polymer electrolyte used for the wet solar battery of this invention. As an amount of the structural unit of ACE expressed with the general formula (1) contained in the above-mentioned copolymer or polymer mixture, or the MCE origin, if it is this copolymer or 20% of the weight or more of polymer mixture, the property of the urethane bond can fully be demonstrated. It is more desirable that it is 50 more % of the weight or more.

[0032] As for the molecular weight of the ACE polymer (aforementioned [M]) contained in the solid polymer electrolyte used for the wet solar battery of this invention, 1 million or less [1000 or more] are desirable, and 50,000 especially or less [5000 or more] are desirable. If the molecular weight of a polymer crosses this range and becomes high, while film properties, such as film reinforcement after processing, will become good, constraint is produced in a thermal motion important for carrier ionic migration, and ion conductivity is reduced, or it is hard coming to melt also into a solvent, and becomes disadvantageous in respect of processing. On the contrary, when molecular weight is too low, membrane formation nature, film reinforcement, etc. will get worse, and a fundamental physical property will be inferior.

[0033] Since MCE or ACE used in order to obtain the ACE polymer (aforementioned [M]) contained in the solid polymer electrolyte used for the wet

solar battery of this invention has one or two polymerization nature machines, a tandem-type macromolecule or a mesh-like macromolecule is obtained by the polymerization. Therefore, by mixing the compound of MCE or ACE suitably, thermal-motion nature is large and film reinforcement can obtain a good polymer. The number of oxyalkylene chains in the oxy-alkyl group used as the side chain of a polymer (namely, R² and [OQ] z in said general formula (1) for example, the number, or n and [OQ] z in said general formula (2) (R³ O) of the oxyalkylene radical contained in inside n in the number of the oxyalkylene radicals contained in inside, or said general formula (3) (R³ O), [Formula 1])



And [OQ] z The number of the oxyalkylene radicals contained in inside has the desirable range of 1-1000, and especially its range of 5-50 is desirable.

[0034] Ionic conductivity of the solid polymer electrolyte used for the wet solar battery of this invention improves further by adding an organic compound as a plasticizer. As an organic compound to add, compatibility with the ACE polymer (aforementioned [M]) is good, a dielectric constant is large, the boiling point is 100 degrees C or more, and the compound with the wide electrochemical stability range is suitable. As such a plasticizer, the sulfur compound of aromatic series nitril, such as carbonate, such as oligo ether, such as triethylene glycol

methyl ether and tetraethylene glycol wood ether, ethylene carbonate, propylene carbonate, diethyl carbonate, and carbonic acid vinylene, a benzonitrile, and torr nitril, dimethylformamide, dimethyl sulfoxide, N-methyl pyrrolidone, N-vinyl pyrrolidone, and sulfolane 66 grade and phosphoric ester are mentioned. In this, oligo ether and carbonate are desirable, and especially carbonate is desirable.

[0035] The ionic conductivity of a solid polymer electrolyte becomes high so that there are many additions of a plasticizer, but if many [too], the mechanical strength of a solid polymer electrolyte will fall. As a desirable addition, it is below the amount of 5 times of (M) ACE polymer weight. Moreover, by using together moderately the compound of polymerization nature like carbonic acid vinylene and N-vinyl pyrrolidone as a plasticizer with a non-polymerization nature plasticizer, and copolymerizing it with ACE or MCE, without reducing a mechanical strength, the addition of a plasticizer is made to increase and ionic conductivity can also be improved.

[0036] As oxidation reduction nature matter used with the ACE polymer (aforementioned [M]) in the solid polymer electrolyte used for the wet solar battery of this invention Although there is also combination with a semiconductor electrode and it is not limited especially, as a general example nS_2/Sn_2 -, nSe_2/Sen_2 -, and nTe_2/Ten_2 - etc. -- chalcogenide / poly chalcogenide ion system, V^{3+}/V^{2+} , Fe^{3+}/Fe^{2+} , and $[Fe(CN)_6]^{3-}/4-$ etc. -- it is mentioned.

Although there is also compatibility with a solid polymer electrolyte and it is not especially limited as such concentration, high concentration is efficiently desirable as much as possible, and to 1l. of solid polymer electrolytes, 0.1 mols or more are dissolved and it is usually used.

[0037] Into the solid polymer electrolyte used for the wet solar battery of this invention, in order to make ion conductivity high, other electrolytes may be added. Especially the class of electrolyte used for compound is not limited, it is desirable for the dissociation constant in the inside of a solid polymer electrolyte to be large, and an alkali-metal salt, quarternary ammonium salt, the 4th class phosphonium salt, a transition-metals salt or proton acid, and various organic acids are mentioned.

[0038] As a class of alkali-metal salt, LiCF_3SO_3 , LiPF_6 , LiClO_4 , LiI , LiBF_4 , LiSCN , LiAsF_6 , NaCF_3SO_3 , NaPF_6 , NaClO_4 , NaI , NaBF_4 , NaAsF_6 , KCF_3SO_3 , KPF_6 , KI , NaOH , LiOH , etc. can be mentioned, for example. As an example of quarternary ammonium salt and the 4th class phosphonium salt, 4 $(\text{CH}_3)\text{NBF}_4$ and 4 $(\text{CH}_3\text{CH}_2)\text{NBF}_4$, $(\text{CH}_3\text{CH}_2)_3\text{NBF}(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4$, 4 $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)\text{NClO}_4$, 4 $(\text{CH}_3)\text{PBF}_4$, and 4 $(\text{CH}_3\text{CH}_2)\text{NBF}_4$ etc. -- it is mentioned.

[0039] as a transition-metals salt -- AgClO_4 , AgI , and CuSO_4 etc. -- it is mentioned. As proton acid and an organic acid, a hydrochloric acid, perchloric acid, fluoroboric acid, a sulfuric acid, an acetic acid, Para toluenesulfonic acid,

trifluoroacetic acid, etc. are mentioned. Although especially an electrolytic mixing ratio is not limited, the rate of one electrolyte molecule is [as opposed to / at the point of ionic conductivity / two - 100 ether oxygen atoms of a side chain] desirable. If the electrolyte used for mixing exists by the larger ratio than one half of ether oxygen atoms, migration of ion is checked greatly, by the ratio conversely smaller than 1/100, the absolute magnitude of ion will become insufficient and ionic conductivity will become small.

[0040] Any of inorganic or an organic semiconductor are sufficient as the semiconductor electrode used for the wet solar battery of this invention. As an inorganic semi-conductor, silicon, gallium phosphorus, a gallium arsenide, indium phosphorus, a copper sulfide indium, a cadmium sulfide, cadmium SERENAIDO, a zinc oxide, the tin oxide, titanium oxide, silicon carbide, a molybdenum sulfide, tungsten SERENAIDO, and these derivatives are mentioned.

[0041] As an organic semiconductor, a porphyrin and its derivative, a phthalocyanine and its derivative, a conductive polymer, etc. are mentioned. As an example of a conductive polymer, the poly arylene vinylenes, those derivatives, etc., such as the poly aniline and its derivative, polyacetylene and its derivative, poly para-phenylene and its derivative, polypyrrole and its derivative, poly thienylene and its derivative, poly pyridine diyl, PORIISO

thianaphthene, poly FURIEN, poly seleno FEN and its derivative, polyphenylene vinylene, poly thienylene vinylene, the poly FURIEN vinylene, the poly NAFUTENIREN vinylene, poly seleno FEN vinylene, and the poly pyridine diyl vinylene, are mentioned.

[0042] Next, an example of the manufacture approach of the wet solar battery of this invention is explained in detail. Conductive matter, such as platinum, gold, indium oxide, and an indium / tin oxide, is used as another electrode, by using as an electrode the semiconductor electrode which formed membranes on the transparent conductive base by vacuum evaporation or the applying method, when only one of the two uses a semiconductor electrode, two poles are put in in the structure for a wet solar-battery configuration so that each other may not be contacted, or it arranges on a base material. For example, two poles are stretched through the spacer of the suitable thickness for the edge of an electrode. At least a kind of polymer or copolymer chosen from ACE or MCE which puts in in said structure and is expressed with a general formula (1) in the meantime, A kind of oxidation reduction nature compound and a kind of electrolyte are mixed at least. Depending on the case Furthermore, after pouring in the polymerization nature monomer mixture which carried out addition mixing and prepared other polymerization nature compounds and/or plasticizers, Carrying out a polymerization by heating and/or electromagnetic wave exposure

etc. for example, by carrying out a polymerization by the polymerization method in the case of obtaining the above-mentioned (M) ACE polymer, and the same approach Or the wet solar battery with which the electrode and the electrolyte contacted good is further obtained by closing by insulating resin, such as an epoxy resin, if needed after a polymerization.

[0043] In addition, when you prepare this polymerization nature monomer mixture, let the ratio of each component to mix be a suitable thing with the wet solar battery made into the purpose. Moreover, the shape of tubed, box-like, and a sheet and what kind of other configurations are sufficient as the configuration of the wet solar battery of this invention. Thus, as an example of the wet solar battery of this invention manufactured, an outline sectional view is shown in drawing 1 . the inside of drawing, and 1 -- an electrode and 2 -- a solid polymer electrolyte and 3 -- a counter electrode and 4 -- a spacer and 5 -- sunlight -- receiving -- the transparent base A and 6 -- lead wire and 7 -- Base B -- it comes out. In addition, an indium / tin oxide / glass transparent electrode is sufficient as the base A of 5, in that case, lead wire 6 is not from a counter electrode 3, and it can be connected to Base A.

[0044]

[Function] In the Kushigata crosslinked polymer which introduced the oxy-alkyl group into the side chain and the bridge formation radical, by introducing a

urethane bond especially into a side chain, film reinforcement of this invention was good and it found out that the above-mentioned problem was solved that a solid polymer electrolyte with high ionic conductivity is obtained, and by using this solid polymer electrolyte for a wet solar battery.

[0045] That is, the solid polymer electrolyte used for the wet solar battery of this invention is a solid electrolyte of high ion conductivity which consists of the Kushigata macromolecule which introduced into the side chain the oxy-alkyl group which has a urethane bond or mesh-like macromolecule which can be easily formed and compounded from the polymerization nature monomer mixture which is the raw material, is good and excellent also in thin film workability. [of film reinforcement] By using said solid polymer electrolyte as ion conductivity matter, processing of thin-film-izing etc. is also easy, the wet solar battery of this invention has high energy efficiency, and it is long lasting. Moreover, according to the manufacture approach of the wet solar battery of this invention, it is possible to be able to manufacture easily in various configurations, for thin-shape-izing of a wet solar battery to be especially easy, and to be able to manufacture the wet solar battery excellent in efficient and long lasting dependability, and to suppose that it is cheap in manufacturing cost.

[0046] When this invention introduced into a side chain the oligo oxy-ethyl group which has a urethane bond in the side chain of the Kushigata crosslinked

polymer of the high molecular compound used as a solid-state solvent, film reinforcement was raised, and ion conductivity could be maintained highly, by using the high molecular compound to apply as a solid-state solvent, processing was also easy, foil did not have fear of a short circuit, either, and that of the ejection current was large, and all reliable solid-state mold cells were developed.

[0047]

[Example] A typical example is shown about this invention below, and it explains to it still more concretely. In addition, these are the mere instantiation for explanation and it cannot be overemphasized that this invention is not what is restricted to these in any way.

[0048] (Example 1)

Composition [of <<2-methacryloiloxy-ethyl carbamic-acid omega-methyl oligo oxy-ethyl ester (MCOA (550))]>>

It sets to [type (2) and they are $R_1 = R_4 = \text{CH}_3$, $R_3 = (\text{CH}_2)_2$, $Q = (\text{CH}_2)_2$, and $Z=1$].

After dissolving 2-methacryloiloxy-ethyl isocyanate (MOI) 0.1mol (15.5g) and monomethyl oligo ethylene glycol 0.1mol (55g) of a mean molecular weight 550 in THF100ml often refined in nitrogen-gas-atmosphere mind, 0.66g dibutyltin dilaurate is added.

[0049] By making it react below 30 degrees C after that for about 3 hours, MCOA

(550) was obtained as colorless viscous liquid. the -- It checked that reacted by 1 to 1, the isocyanate radical of MOI disappeared further, and the urethane bond was generating MOI and monomethyl oligo ethylene glycol from the result of 1 H-NMR, IR, and ultimate analysis.

[0050] Composition [of <<2-acryloyloxyethyl carbamic-acid 2-acryloyloxyethyl carbamoyl oligo OKISHIECHIRU ester (ACAC (1000))]>>

[-- a formula (2) -- setting -- $R1 = H$, $R3 = (CH_2)_2$, $R4 = CONH(CH_2)_2$ $OCOCH=CH_2$, $Q = (CH_2)_2$, and $Z=1$]

After dissolving 2-acryloyloxyethyl isocyanate (AOI) 0.2mol (28.2g) and oligo ethylene glycol 0.1mol (100g) of a mean molecular weight 1000 in THF100ml often generated in nitrogen-gas-atmosphere mind, 0.66g dibutyltin dilaurate is added. Then, ACAC (1000) was obtained as colorless viscous liquid by making it react at 50 degrees C for about 3 hours. the -- It checked that reacted by 2 to 1, the isocyanate radical of AOI disappeared further, and the urethane bond was generating AOI and oligo ethylene glycol from 1 H-NMR, IR, and ultimate analysis.

[0051] Production and evaluation>> of a <<MCOA(550)/ACAC (1000) copolymerization system solid polymer electrolyte MCOA(550)2.00g compounded above, ACAC(1000) 0.80g compounded in the example 2, NaBF₄ 0.2g, NaI 0.2g, and I₂ 0.02g were dissolved in (propylene carbonate PC) 7g, and

the monomer mixture for solid polymer electrolytes was obtained as viscous liquid. Under argon atmosphere, when this mixture was heated at 100 degrees C after applying in the shape of a glass plate for 1 hour, a MCOA(550)/ACAC (1000) copolymer / NaBF₄ / NaI/PC complex was obtained as about 100-micrometer transparent film. When whenever [25-degree C ionic conduction / of this film] was measured in the impedance method, it was 3x10⁻³ S/cm.

[0052] <Manufacture of Cd (Se, Te) photoelectrical pole> Journal OBU 132 volumes and the approach reported by 1077 pages will be followed in an electrochemical society and 1985, and they are CdSO₄, SeO₂, and TeO₂ on a 4x5cm titanium electrode. From the sulfuric-acid water solution, Cd (Se, Te) photoelectrical pole with a thickness of about 1 micrometer was manufactured by carrying out electrocrystallization.

[0053] <Manufacture of a wet solar battery and evaluation> After applying the monomer mixture for giant-molecule solid electrolytes which covered with the 5-micrometer polyimide film about 1mm four way type of edges of Cd (Se, Te) photoelectrical pole which manufactured above, next was prepared in the example 3, commercial indium / tin oxide / glass transparent electrode were piled up, and the wet solar battery using a solid polymer electrolyte as shown in drawing 1 was manufactured by subsequently heating at 100 degrees C for 1

hour. The open-circuit voltage at the time of irradiating for 1 hour, using the tungsten halogen lamp of 500W as the light source was 0.4V. Moreover, in an open circuit, they are 0.1 mA/cm². It turned out that the current for 30 minutes or more flows, and it is operating as a photoelectric cell.

[0054] (Example 2)

Composition [of <<methacryloyl oligo carbamic-acid ester (MOC (750)) >>]>>

[-- a formula (3) -- setting -- R1 = -- CH₃, R3 =(CH₂)², and R4 = -- CH₃, R5=(CH₂)⁶, R6 =(CH₂)², Q= (CH₂)², n= 3, and Z= 1 --]

After dissolving hexamethylene diisocyanate 0.1mol (16.8g), polyethylene-glycol 0.1mol (40g) of a mean molecular weight 400, and triethylene glycol monomethyl ether 0.1mol (16.4g) in THF100ml often refined in nitrogen-gas-atmosphere mind, 0.66g dibutyltin dilaurate is added. Then, the colorless viscous liquid product was obtained by making it react at 60 degrees C for about 1 hour. the -- The result of ¹H-NMR and IR showed that the isocyanate radical of hexamethylene diisocyanate disappeared and the urethane bond was generating. Moreover, in the result of this GPC, the average molecular weight of polyethylene-glycol conversion of the obtained product was about 750.

[0055] After dissolving in THF100ml which often refined again 75g of compounds, and 2-methacryloiloxy-ethyl isocyanate (MOI) 0.1mol (15.5g) obtained by the above-mentioned approach in nitrogen-gas-atmosphere mind,

0.66g dibutyltin dilaurate is added. Then, the product was obtained as colorless viscous liquid by making it react at 50 degrees C for about 3 hours. The result of $^1\text{H-NMR}$, IR, and elemental analysis showed that the isocyanate radical of MOI had disappeared and the urethane bond was increasing.

[0056] This monomer 2.69g could be dissolved in THF 10cc, LiCF_3SO_3 0.14g could be added, and it mixed. Subsequently, when this solution was heated at 100 degrees C after applying on the bottom glass plate of argon atmosphere for 1 hour, it was obtained as about 100-micrometer transparent independence film. When the 25-degree C ionic conductivity of this film was measured in the impedance method, it was $1 \times 10^{-5} \text{ S/cm}$.

[0057] Composition [of <<screw acryloyl oligo carbamic-acid ester (BAC (1000)) >>]>>

[-- a formula (3) -- setting -- $\text{R}_1 = \text{H}$ and $\text{R}_3 = (\text{CH}_2)_2$, $\text{R}_4 = \text{CONH}(\text{CH}_2)_2\text{OCOCH}=\text{CH}_2$, $\text{R}_5 = (\text{CH}_2)_6$, $\text{R}_6 = (\text{CH}_2)_2$, $\text{Q} = (\text{CH}_2)_2$, and $\text{Z} = 1$ --]

After dissolving hexamethylene diisocyanate 0.1mol (16.8g) and polyethylene-glycol 0.2mol (80g) of a mean molecular weight 400 in THF 100ml often refined in nitrogen-gas-atmosphere mind, 0.66g dibutyltin dilaurate is added. Then, the white solid-state product was obtained by making it react at 60 degrees C for about 1 hour. The result of $^1\text{H-NMR}$ and IR showed that the isocyanate radical of hexamethylene diisocyanate disappeared and the urethane

bond was generating. Moreover, in the result of this GPC, the average molecular weight of polyethylene-glycol conversion of the obtained product was about 1000.

[0058] After dissolving 50g of this compound, and 2-acryloyloxyethyl isocyanate (AOI) 0.1mol (14.1g) in THF100ml often again refined in nitrogen-gas-atmosphere mind, 0.66g dibutyltin dilaurate is added. Then, the product was obtained as a white solid-state by making it react at 50 degrees C for about 3 hours. the -- The result of ¹H-NMR, IR, and elemental analysis showed that the isocyanate radical of AOI had disappeared and the urethane bond was increasing.

[0059] Production and evaluation>> of a <<MOC(750)/BAC (1000) copolymerization system solid polymer electrolyte MOC(750) 2.69g compounded above and BAC(1000) 0.74g, NaBF₄ 0.2g, NaI 0.2g, and I₂ 0.02g were dissolved in (propylene carbonate PC) 7g, and the monomer mixture for solid polymer electrolytes was obtained as viscous liquid. Under argon atmosphere, when this mixture was heated at 100 degrees C after applying on a glass plate for 1 hour, the plasticization solid polymer electrolyte was obtained as about 300-micrometer transparent independence film. When the 25-degree C ionic conductivity of this film was measured in the impedance method, it was 1x10⁻³ S/cm.

[0060] <Manufacture of a wet solar battery and evaluation> After applying the monomer mixture for giant-molecule solid electrolytes which covered with the 5-micrometer polyimide film about 1mm four way type of edges of Cd (Se, Te) photoelectrical pole which manufactured in the example 1, next was prepared above, commercial indium / tin oxide / glass transparent electrode were piled up, and the wet solar battery using a solid polymer electrolyte as shown in drawing 1 was manufactured by subsequently heating at 100 degrees C for 1 hour. The open-circuit voltage at the time of irradiating for 1 hour, using the DANGU stainless steel-halogen lamp of 500W as the light source was 0.4V. Moreover, in a closed circuit, they are 0.1 mA/cm². It turned out that the current for 30 minutes or more flows, and it is operating as a photoelectric cell.

[0061] (Example 3)

Composition [of <<methacryloyl carbamic-acid omega-methyl oligo oxy-ethyl ester (MCA (550))]>>

It sets to [type (2) and they are R1 =CH₃, R3 =(CH₂)², R4 =CH₃, and Z=0].

After dissolving methacryloyl isocyanate (MAI) (Nippon Paint Co., Ltd. make) 0.1mol (11.1g) and monomethyl oligo ethylene glycol 0.1mol (55g) of a mean molecular weight 550 in THF100ml often refined in nitrogen-gas-atmosphere mind, 0.66g dibutyltin dilaurate is added.

[0062] By making it react below 30 degrees C after that for about 3 hours, MCA

(550) was obtained as colorless viscous liquid. the -- It checked that reacted by 1 to 1, the isocyanate radical of MAI disappeared further, and the urethane bond was generating MAI and monomethyl oligo ethylene glycol from the result of 1 H-NMR, IR, and ultimate analysis.

[0063] Composition [of <<methacryloyl carbamic-acid methacryloyl carbamoyl oligo (oxy-ethyl / oxy-propyl) ester (MCM (800))]>>

[-- a formula (2) -- setting -- R1 =CH3, R3 = {CH(CH3) CH2 and -(CH2) 2-} R4 =CONHCOC(CH3) =CH2, Z= 0, and w= 0 --]

After dissolving methacryloyl isocyanate (MAI) 0.2mol (22.2g) and 0.1 mols (80g) of the ethylene glycol / propylene glycol random copolymers of a mean molecular weight 800 in THF100ml often generated in nitrogen-gas-atmosphere mind, 0.66g dibutyltin dilaurate is added. Then, MCM (800) was obtained as colorless viscous liquid by making it react at 50 degrees C for about 3 hours. the -- It checked that MAI, and ethylene glycol / propylene glycol copolymer reacted by 2 to 1, the isocyanate radical of MAI disappeared further, and the urethane bond was generating from 1 H-NMR, IR, and ultimate analysis.

[0064] Production and evaluation>> of a <<MCA(550)/MCM (800) copolymerization system solid polymer electrolyte MCA(550)1.80g compounded above, MCM(800) 0.60g compounded in the example 2, NaBF4 0.2g, NaI0.2g, and I2 0.02g were dissolved in (propylene carbonate PC) 7g, and the monomer

mixture for solid polymer electrolytes was obtained as viscous liquid. Under argon atmosphere, when this mixture was heated at 100 degrees C after applying on a glass plate for 1 hour, MCA (550) / MCM (800) copolymer / NaBF₄ / NaI/PC complex was obtained as about 100-micrometer transparent film. When [25-degree C ionic conduction / of this film] was measured in the impedance method, it was 1×10^{-3} S/cm.

[0065] <Manufacture of a wet solar battery and evaluation> After applying the monomer mixture for giant-molecule solid electrolytes which covered with the 5-micrometer polyimide film about 1mm four way type of edges of Cd (Se, Te) photoelectrical pole which manufactured in the example 1, next was prepared above, commercial indium / tin oxide / glass transparent electrode were piled up, and the wet solar battery using a solid polymer electrolyte as shown in drawing 1 was manufactured by subsequently heating at 100 degrees C for 1 hour. The open-circuit voltage at the time of irradiating for 1 hour, using the tungsten halogen lamp of 500W as the light source was 0.4V. Moreover, in a closed circuit, they are 0.1 mA/cm². It turned out that the current for 30 minutes or more flows, and it is operating as a photoelectric cell.

[0066]

[Effect of the Invention] It consists of complex of at least the macromolecule which has the oxy-alkyl group combined by the urethane bond in a side chain,

and a kind of electrolyte, and film reinforcement is easy to be obtained as a good thin film, and the solid polymer electrolyte used for the wet solar battery of this invention has the description of high ion conductivity.

[0067] Since the ion conductivity matter of the wet solar battery of this invention using the above-mentioned solid polymer electrolyte is a solid-state, there is neither corrosion of an electrode nor risk of a liquid spill, and it can use it, being stabilized for a long period of time. Moreover, a wet solar battery thin by making a solid polymer electrolyte layer form by the applying method can be manufactured simple.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline sectional view of one example of the thin solid-state wet solar battery shown as an example of the wet solar battery by this invention.

[Description of Notations]

1 Electrode

2 Solid Polymer Electrolyte

3 Counter Electrode

4 Spacer

5 Base A

6 Lead Wire

7 Base B



中华人民共和国国家知识产权局

邮政编码: 200233 上海桂平路 435 号 上海专利商标事务所有限公司 周承泽		发文日期
申请号: 038109018		
申请人: 索尼株式会社		
发明创造名称: 固体电解质, 光电装置及其制造方法		

第一次审查意见通知书

(进入国家阶段的 PCT 申请)

1. ☐ 应申请人提出的实审请求, 根据专利法第 35 条第 1 款的规定, 国家知识产权局对上述发明专利申请进行实质审查。

☐ 根据专利法第 35 条第 2 款的规定, 国家知识产权局专利局决定自行对上述发明专利申请进行审查。

2. ☒ 申请人要求以其在:

JP 专利局的申请日 2002 年 04 月 11 日为优先权日
专利局的申请日 年 月 日为优先权日
专利局的申请日 年 月 日为优先权日

3. ☐ 申请人于 年 月 日提交的修改文件, 不符合专利法实施细则第 51 条的规定。

☐ 申请人提交的下列修改文件不符合专利法第 33 条的规定。

☐ 国际初步审查报告附件的中文译文。

☐ 依据专利合作条约第 19 条规定所提交的修改文件的中文译文。

☐ 依据专利合作条约第 28 条或 41 条规定所提交的修改文件。

☐

4. ☒ 审查是针对原始提交的国际申请的中文译文进行的。

☐ 审查是针对下述申请文件进行的:

☐ 说明书 第 页, 按照原始提交的国际申请文件的中文译文;

第 页, 按照国际初步审查报告附件的中文译文;

第 页, 按照依据专利合作条约第 28 条或 41 条规定所提交的修改文件;

第 页, 按照依据专利法实施细则第 51 条规定所提交的修改文件。

☐

☐ 权利要求 第 项, 按照原始提交的国际申请文件的中文译文;

第 项, 按照依据专利合作条约第 19 条规定所提交的修改文件的中文译文。

第 项, 按照国际初步审查报告附件的中文译文;

第 项, 按照依据专利合作条约第 28 条或 41 条所提交的修改文件;

第 项, 按照依据专利法实施细则第 51 条规定所提交的修改文件。

☐

☐ 附图 第 页, 按照原始提交的国际申请文件的中文译文;

第 页, 按照国际初步审查报告附件的中文译文;

第 页, 按照依据专利合作条约第 28 条或 41 条所提交的修改文件;

第 页, 按照依据专利法实施细则第 51 条规定所提交的修改文件。

21302
2002. 8



回函请寄: 100088 北京市海淀区蓟门桥西土城路 6 号 国家知识产权局专利局受理处收
(注: 凡寄给审查员个人的信函不具有法律效力)

申请号 038109018

☐

☒ 本通知书引用下述对比文献(其编号在今后的审查过程中继续沿用):

编号	文件号或名称	公开日期(或抵触申请的申请日)
1	J18-88030A	1996-04-02
2	J12001-110462A	2001-04-20
3	J12000-306605A	2000-11-02

5. 审查的结论性意见:

☐ 关于说明书:

- ☐ 申请的内容属于专利法第 5 条规定的不授予专利权的范围。
- ☐ 说明书不符合专利法第 26 条第 3 款的规定。
- ☐ 说明书不符合专利法第 33 条的规定。
- ☐ 说明书的撰写不符合专利法实施细则第 18 条的规定。

☒ 关于权利要求书:

- ☒ 权利要求 1-5, 8-11, 13, 14 不具备专利法第 22 条第 2 款规定的新颖性。
- ☒ 权利要求 6, 7, 12 不具备专利法第 22 条第 3 款规定的创造性。
- ☐ 权利要求 不具专利法第 22 条第 4 款规定的实用性。
- ☐ 权利要求 属于专利法第 25 条规定的不授予专利权的范围。
- ☐ 权利要求 不符合专利法第 26 条第 4 款的规定。
- ☐ 权利要求 不符合专利法第 31 条第 1 款的规定。
- ☐ 权利要求 不符合专利法第 33 条的规定。
- ☐ 权利要求 不符合专利法实施细则第 13 条第 1 款的规定。
- ☐ 权利要求 不符合专利法实施细则第 2 条第 1 款关于发明的定义。
- ☐ 权利要求 不符合专利法实施细则第 20 条的规定。
- ☐ 权利要求 不符合专利法实施细则第 21 条的规定。
- ☐ 权利要求 不符合专利法实施细则第 22 条的规定。
- ☐ 权利要求 不符合专利法实施细则第 23 条的规定。

上述结论性意见的具体分析见本通知书的正文部分。

6. 基于上述结论性意见, 审查员认为:

- ☐ 申请人应按照通知书正文部分提出的要求, 对申请文件进行修改。
- ☐ 申请人应在意见陈述书中论述其专利申请可以被授予专利权的理由, 并对通知书正文部分中指出的不符合规定之处进行修改, 否则将不能授予专利权。
- ☒ 专利申请中没有可以被授予专利权的实质性内容, 如果申请人没有陈述理由或者陈述理由不充分, 其申请将被驳回。

7. 申请人应注意下述事项:

- (1) 根据专利法第 37 条的规定, 申请人应在收到本通知书之日起的肆个月内陈述意见, 如果申请人无正当理由逾期不答复, 其申请将被视为撤回。
- (2) 申请人对其申请的修改应符合专利法第 33 条的规定, 修改文本应一式两份, 其格式应符合审查指南的有关规定。
- (3) 申请人的意见陈述书和 / 或修改文本应邮寄或递交国家知识产权局专利局受理处, 凡未邮寄或递交给受理处的文件不具备法律效力。
- (4) 未经预约, 申请人和 / 或代理人不得前来国家知识产权局专利局与审查员举行会晤。

8. 本通知书正文部分共有 4 页, 并附有下列附件:

- ☒ 引用的对比文件的复印件共 3 份 38 页。

审查员: 徐红彬(9258)
2006 年 10 月 10 日

审查部门

审查协作中心

21302
2002.8



回函请寄: 100088 北京市海淀区蓟门桥西土城路 6 号 国家知识产权局专利局受理处收
(注: 凡寄给审查员个人的信函不具有法律效力)

第一次审查意见通知书正文

本申请涉及一种固体电解质、光电装置及其制造方法。经实质审查, 作出如下审查意见:

权利要求 1 请求保护一种包含电解质组合物和母体聚合物的电解质。对比文件 1 (JP8-88030A) 公开了一种湿式太阳电池及其制造方法, 其中 (参见说明书第 5 页第【0021】节至第 7 页第【0046】节) 披露了如下一种包含电解质组合物和母体聚合物的电解质, 该母体聚合物是由具至少 2 个异氰酸酯基团的第一化合物和具至少 2 个活性氢亲核基团的第二化合物聚合形成。

通过比较知, 对比文件 1 公开了权利要求 1 的全部技术特征。两者技术领域相同, 所要解决的技术问题相同, 采用了相同的技术手段, 并能达到相同的技术效果。因此, 权利要求 1 相对于对比文件 1 不具备专利法第二十二条第二款规定的新颖性。

权利要求 2 引用了权利要求 1, 附加技术特征为: 该电解质组合物包含形成凝胶电解质的溶剂。该特征已经被对比文件 1 (说明书第【0029】节) 所披露。因此, 当权利要求 1 不具备新颖性时, 权利要求 2 不具备专利法第二十二条第二款规定的新颖性。

权利要求 3 引用了权利要求 1, 附加技术特征为: 该电解质组合物不包含形成固体电解质的溶剂。该特征已经被对比文件 1 (说明书【0027】) 所披露。因此, 当权利要求 1 不具备新颖性时, 权利要求 3 不具备专利法第二十二条第二款规定的新颖性。

权利要求 4 引用了权利要求 1, 附加技术特征为: 该电解质组合物包含形成凝胶电解质的离子液体。该特征已经被对比文件 1 (说明书【0028】节) 所披露。因此, 当权利要求 1 不具备新颖性时, 权利要求 4 不具备专利法第二十二条第二款规定的新颖性。

权利要求 5 引用了权利要求 1, 附加技术特征为: 该电解质组合物包含氧化还原偶。该特征已经被对比文件 1 (说明书【0028】节) 所披露。因此, 当权利要求 1 不具备新颖性时, 权利要求 5 不具备专利法第二十二条第二款规定的新颖性。

权利要求 6 引用了权利要求 5, 附加技术特征为: 该氧化还原偶是卤素离子和卤化物离子的结合。对比文件 2 (JP2001-110462A) 公开了一种光电变换元件及其制造方法, 其中 (说明书第【0042】至【0047】节) 披露了在制造电解质过程中使用“卤素离子和卤化物离子”结合的氧化还原偶。对比文件 2 中披露的内容与在权利要求 6 中的作用相同。对于所属技术领域的技术人员来说, 对比文件 2 给出了将其公开的上述内容用于对比文件 1 以解决其技术问题 (使用合适溶剂) 的启示, 也就是说, 由对比文件 1 结合对比文件 2 得到权利要求 6 的技术方案是显而易见的。因此, 权利要求 6 相对于对比文件 1 和 2 不具备专利法第二十二条第三款规定的创造性。

权利要求 7 引用了权利要求 6, 附加技术特征为: 该氧化还原偶的律诉元素是碘。该特征已经被对比文件 2 (说明书【0042】节) 所披露。因此, 当权利要求 6 不具备创造性时, 权利要求 7 不具备专利法第二十二条第三款规定的创造性。

权利要求 8 请求保护一种光电池。对比文件 3 (JP2000-306605A) 公开了一种高线性硬化活性的高分子固体电解质及其制造方法, 其中 (参见附图 1 以及说明书第【0056】至【0108】节) 披露了如下一种光电池: 包括载有染料的半导体颗粒组成的半导体层 (说明书第【0108】节) 和电解质层 (附图标记 2), 这些层位于反电极和基底表面上形成的电极之间 (附图 1), 其中电解质层具有氧化还原偶 (说明书第【0056】节)、电解质组合物和母体聚合物, 该母体聚合物是由具至少 2 个异氰酸酯基团 (说明书第【0058】节) 的第一化合物和具至少 2 个含活性氢亲核基团 (说明书第【0056】) 的第二化合物聚合形成的聚合物。

通过比较知, 对比文件 3 公开了权利要求 8 的全部技术特征。两者技术领域相同, 所要解决的技术问题相同, 采用了相同的技术手段, 并能达到相同的技术效果。因此, 权利要求 8 相对于对比文件 3 不具备专利法第二十二条第二款规定的新颖性。

权利要求 9 引用了权利要求 8, 附加技术特征为: 基底是透明基底。该特征已经被对比文件 3 (说明书第【0125】节) 所披露。因此, 当权利要求 8 不具备新颖性时, 权利要求 9 不具备专利法第二十二条第二款规定的新颖性。

权利要求 10 请求保护一种制造光电池的方法。对比文件 3 (参见附图 1 以及说明书第【0056】至【0108】节) 披露了如下一种制造光电池的方法, 包括步骤:

在反电极和基底表面形成的电极之间注入混合溶液, 混合物含有具至少 2 个异氰酸酯基团 (说明书第【0058】节) 的第一化合物和具至少 2 个含活性氢亲核基团 (说明书第【0056】) 的第二化合物以及具氧化还原偶的电解质组合物; 并将第一化合物和第二化合物聚合。

通过比较知, 对比文件 3 公开了权利要求 10 的全部技术特征。两者技术领域相同, 所要解决的技术问题相同, 采用了相同的技术手段, 并能达到相同的技术效果。因此, 权利要求 10 相对于对比文件 3 不具备专利法第二十二条第二款规定的新颖性。

权利要求 11 引用了权利要求 10, 附加技术特征为: 还进一步包括在电极和反电极之间形成由载有染料半导体颗粒组成的半导体层的步骤。该特征已经被对比文件 3 (说明书第【0108】节) 所披露。因此, 当权利要求 10 不具备新颖性时, 权利要求 11 不具备专利法第二十二条第二款规定的新颖性。

权利要求 12 引用了权利要求 10, 附加技术特征为: 聚合是根据 Michael 加成反应进行的。该特征属于本领域公知常识。因此, 当权利要求 10 不具备新颖性时, 权利要求 12 不具备专利法第二十二条第三款规定的创造性。

权利要求 13 引用了权利要求 10, 附加技术特征为: 电解质组合物有氧化还原偶。该特征已经被对比文件 3 (说明书第【0056】节) 所披露。因此, 当权利要求 10 不具备新颖性时, 权利要求 13 不具备专利法第二十二条第二款规定的新颖性。

权利要求 14 请求保护一种制造光电池的方法。对比文件 3 (参见附图 1 以及说明书第【0056】至【0108】节) 披露了如下一种制造光电池的方法, 包括步骤: 在反电极和基底表面形成的电极之间形成载有染料半导体颗粒组合的半导体层; 加入具至少 2 个异氰酸酯基团 (说明书第【0058】节) 的第一化合物和具至少 2 个含活性氢亲核基团 (说明书第【0056】) 的第二化合物; 并聚合第一化合物和第二化合物。

通过比较知, 对比文件 3 公开了权利要求 14 的全部技术特征。两者技术领域相同, 所要解决的技术问题相同, 采用了相同的技术手段, 并能达到相同的技术效果。因此, 权利要求 14 相对于对比文件 3 不具备专利法第二十二条第二款规定的新颖性。

基于上述理由，权利要求 1-5、8-11、13、14 不具备新颖性，权利要求 6、7、12 不具备创造性，并且在其说明书中没有记载任何相对于对比文件 1 和或 2、对比文件 3 具有专利性的实质性内容，因此，即使申请人对权利要求进行重新组合和/或根据说明书记载的内容作出进一步的限定，本申请也不具备被授予专利权的前景。如果申请人不能在本通知书指定的答复期限内提出表明本申请具有新颖性和创造性的充分理由，按照专利法第三十八条的规定，本申请将被驳回。